WHAT CONSTITUTES SUCCESS IN THE TRANSFER FROM THE LAB TO THE FIELD?

John T. Wilson

U.S. Environmental Protection Agency
Robert S. Kerr Environmental Research Laboratory
Ada, OK 74820

November 1992

ENVIRONICS DIVISION
Civil Engineering Laboratory

■ **Air Force Civil Engineering Support Agency**   ■ **Tyndall Air Force Base, FL 32403-5323**

DISCLAIMER

Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not constitute or imply its endorsement, recommendation, or approval by the United States Air Force. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Air Force.

This report was prepared as an account of work sponsored by the United States Air Force. Neither the United States Air Force, nor any of its employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights

This document is submitted as an historical record of work performed. Limitations of the available media rendered editing impractical; therefore it is retained "as is."

REPORT DOCUMENTATION PAGE

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
30-NOV-1992	Book Chapter - PREPRINT	30-NOV-1989 -- 30-NOV-1992

4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER
What Constitutes Success in the Transfer from the Lab to the Field? (PREPRINT)	
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)	5d. PROJECT NUMBER
Wilson, John T.	
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
	19007074

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)	8. PERFORMING ORGANIZATION REPORT NUMBER
Environmental Protection Agency Robert S. Kerr Environmental Research Laboratory Ada, OK 74820	

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S)
Air Force Research Laboratory Materials and Manufacturing Directorate Airbase Technologies Division 139 Barnes Drive, Suite 2 Tyndall Air Force Base, FL 32403-5323	
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)
	ESL-TP-1992-302

12. DISTRIBUTION/AVAILABILITY STATEMENT
Distribution Statement A: Approved for public release; distribution unlimited.
Available only to DTIC users. U.S. Government or Federal Purpose Rights License.

13. SUPPLEMENTARY NOTES
Distribution Code 20: JOURNAL ARTICLES; DTIC USERS ONLY. Document contains color images. Submitted to National Academy Press for publication in National Research Council's book, "In Situ Bioremediation. When Does It Work?"

14. ABSTRACT

An operational definition for success at field scale would include meeting regulatory goals for ground water quality in a timely fashion, and at a predictable cost. Current practice for site characterization does not adequately define the amount of contamination subject to bioremediation. As a result, estimates of the requirements for electron acceptors and mineral nutrients, and the time required for remediation, have much uncertainty. In contrast to laboratory studies, the extent of remediation achieved at field scale is influenced by dilution of compounds of regulatory concern in circulated water, and by partitioning of the regulated compounds between water and residual oily phase material. Current practice fails to distinguish reduction in concentration due to dilution and partitioning from reductions caused by biodegradation. Another aspect of success is the capacity to continue to meet regulatory goals for ground water quality after the active phase of remediation is complete. The extent of weathering of residual oily phase materials, and the hydrological environment occupied by the residual, has a strong influence on the potential for ground water contamination after active remediation ceases.

15. SUBJECT TERMS

in situ remediation

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Bruce Nielsen
U	U	U	UU	35	19b. TELEPHONE NUMBER *(Include area code)*

Reset

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39.18

In Situ Bioremediation: How Do We Know When It Works?

What Constitutes Success in the Transfer from the Lab to the Field?

John T. Wilson

R.S. Kerr Laboratory (U.S. EPA)

Ada, Oklahoma

An operational definition for success at field scale would include meeting regulatory goals for ground water quality in a timely fashion, and at a predictable cost. Current practice for site characterization does not adequately define the amount of contamination subject to bioremediation. As a result, estimates of the requirements for electron acceptors and mineral nutrients, and the time required for remediation, have much uncertainty. In contrast to laboratory studies, the extent of remediation achieved at field scale is influenced by dilution of compounds of regulatory concern in circulated water, and by partitioning of the regulated compounds between water and residual oily phase material. Current practice fails to distinguish reduction in concentration due to dilution and partitioning from reductions caused by biodegradation. Another aspect of success is the capacity to continue to meet regulatory goals for ground water quality after the active phase of remediation is complete. The extent of weathering of residual oily phase material, and the hydrological environment occupied by the residual, has a strong influence on the potential for ground water contamination after active remediation ceases.

BIOREMEDIATION AS A PROCESS AND A TECHNOLOGY

Transfer of bioremediation laboratory research to the field is often a frustrating and unsatisfying activity. Part of the problem has to do with the level of inquiry in the laboratory and in the field. Laboratory studies deal with biochemical or physiological processes. Appropriate controls insure that only one mechanism is responsible for the phenomena under study. During field scale implementation of bioremediation technology, several processes operate concurrently. There may be several distinct mechanisms for biological destruction of the contaminant, as well as partitioning to immobile phases, dilution in ground water, and volatilization.

Experimental controls are usually unavailable during full scale implementation of in situ bioremediation, because the technology is applied uniformly to the contaminated area. As a result, performance monitoring that is limited to the concentration of contaminants in ground water over time, and perhaps the concentration of nutrients and electron acceptors, gives no surety that the biological process developed in the laboratory was responsible for contaminant removal at full scale.

The appropriate equivalent of experimental controls is a detailed site characterization, and detailed characterization of the flow of remedial fluids and flux of amendments. This characterization allows an assessment of the influence of partitioning, dilution, or volatilization, and provides a basis for an evaluation of the relative contribution of bioremediation.

APPROPRIATE SITE CHARACTERIZATION

Most plumes of organic contamination in ground water originate from spills of refined petroleum hydrocarbons, such as gasoline, or chlorinated solvents, such as trichloroethylene. As long as the oily phase liquid is present in the subsurface, it can act as a continuing source of ground water contamination.

Traditionally, monitoring wells have been used to define the extent of contamination in the subsurface environment. However, wells are incapable of determining the extent of contamination by oily phase materials. If monitoring well data are the only data available, it is difficult to estimate the total contaminant mass subject to remediation within an order of magnitude.

As an example, Kennedy and Hutchins (1992) estimated the mass of alkylbenzenes released to a shallow water table aquifer from a pipeline spill of refined petroleum product. The contaminated area was roughly circular with a diameter of 150 meters. Thirteen monitoring stations were located uniformly across the spill. At each station a series of continuous cores were taken extending from clean material above the spill, through the spill to clean material below it. Then a monitoring well was installed in the borehole used to acquire the cores.

The cores were extracted an analyzed for the content of benzene, BTEX compounds, and Total Petroleum Hydrocarbons. Ground water was collected and analyzed for the same parameters. Data from the thirteen stations was subjected to geostatistical analysis to estimate the total contaminant mass in the aquifer, and the total mass dissolved in the ground water. Of 320 kg of benzene in the aquifer, only 22 kg was dissolved in the ground water; of 8,800

kg of BTEX compounds, only 82 kg was dissolved; and of 390,000 kg of Total Petroleum Hydrocarbons, only 115 kg was dissolved. Site characterization techniques are required that can accurately estimate the total mass of contaminants subject to bioremediation.

Estimates of Total Contaminant Mass

Estimates of the total contaminant mass in the subsurface are required to predict the demand for nutrients and electron acceptor that must be met to complete the remediation. If the total demand of nutrients and electron acceptor has been estimated, the rate of supply of the limiting requirement can be used to estimate the time required for remediation.

The most rigorous approach involves the collection of cores from the contaminated regions of the subsurface environment, followed by extraction and analysis of the cores for the contaminants of concern. Use of a wireline piston sampler (Zapico et al. 1987) makes it possible to collect representative continuous cores, even in non-cohesive material. Current good practice does not recommend shipping core samples to a laboratory for extraction. If the cores are subsampled and extracted in the field, the variability between replicate subsamples is much smaller (Siegrist and Jenssen, 1990).

At present, this approach is too expensive to be practical for general use. The data set reported by Kennedy and Hutchins (1992) contained over four hundred analyses. However, there are several techniques that can reduce the analytical burden. Often headspace analysis of cores collected in the field has a strong correlation to content of total petroleum hydrocarbons. Headspace techniques can be used to screen cores in the field to determine

4

whether the depth interval represented by a core is contaminated, and extraction and analysis of the core is justified.

Aquifer samples can be equilibrated with the headspace of a plastic bag before analysis by a field gas chromatograph, organic vapor analyzer, or explosimeter (Robbins et al., 1989). Alternately, a plug can be removed from a core with a paste sampler, and the inlet to the explosimeter or organic vapor analyzer can be inserted directly into the cavity (Kampbell and Cook, 1992). These techniques are inexpensive, and generate data in real time. This allows the screening information to be used to guide decisions about depth and location of subsequent cores.

If a correlation can be established between the meter response of a head space anslysis and the content of total petroleum hydrocarbons, results from a limited number of expensive core analyses can be extrapolated to a large number of inexpensive field headspace analyses. Kampbell and Cook (1992) reported correlation coefficients between meter response and hydrocarbon content of 0.957 on a set of 24 cores, and 0.801 on a set of 64 cores.

Estimates of Contaminant Dilution in Ground Water

In the process of remediation, prodigious quantities of water may be circulated through an oily phase spill. The compounds of regulatory concern, such as the BTEX compounds, are often more water soluble than the other components of refined petroleum hydrocarbons. As the circulated water sweeps through the spill, the more water soluble components partition into the water and are diluted out. The concentration of regulated compounds will drop due

to simple dilution. Downs et al. (1989, 1993) quantitatively described this effect in a pilot scale demonstration of in situ bioremediation of a jet fuel spill using nitrate as the electron acceptor. They used a tracer to estimate the volume of recirculated water, cored the area perfused by ground water to estimate the quantity of total hydrocarbons, and the quantity of hydrocarbons of regulatory concern. Simple partitioning theory was used to calculate the distribution of hydrocarbons of concern between recirculating ground water and the residual jet fuel.

Estimate of recirculated volume of water

An infiltration gallery installed above the spill effectively perfused a plan surface area of 130 square meters with water supplemented with nitrate and mineral nutrients. The infiltrated water was recovered in five purge wells. See figure 1 for a computer model predicting flow paths from the infiltration gallery to the recovery wells. See figure 2 for a cross section showing the relation of the infiltration gallery, the contaminated interval, and the recovery wells. A pulse of chloride was used to trace the flow of water to the recovery wells. The volume of circulated water was considered to be the pumping rate multiplied by the travel time of the chloride between infiltration and the recovery wells. The arrival time at each well was weighted by its pumping rate to calculate the overall residence time, and circulated volume, between infiltration and recovery. See figure 3 for breakthrough curves of the chloride tracer.

In the demonstration, the average residence time was 10 days and the circulated volume was 10,900 cubic meters.

Estimate of partitioning between oil and water

The area of the spill that was perfused by the infiltration gallery had been cored to determine the total quantity of jet fuel, and the quantities of benzene, toluene, ethylbenzene, and the xylene. Smith et al. had reported empirical partition coefficients for the compounds between JP-4 jet fuel and water. To estimate the distribution of an individual BTEX compound between fuel and water, the published partition coefficients were multiplied by the ratio of the volume of JP-4 under the infiltration gallery to the volume of water in the circulation. The distribution between oil and fuel was used to calculate the fraction of total material in oil or water. To predict the equilibrium solution concentration of a BTEX compound in the circulation, the quantity of the compound originally present in the fuel was multiplied by the fraction that should partition to water, and divided by the circulated volume of ground water.

Table I compares the predicted dilution of benzene, toluene, and o-xylene to the actual concentration in monitoring wells prior to recirculation of ground water. Dilution alone produced at least a five-fold reduction in concentration.

To maintain hydraulic control over the spill, a fraction of the recovered water was discharged to waste. This flow was replaced with clean water recruited from the aquifer. If the circulation system behaved as a completely mixed reactor, solutes in the circulated water would be removed at a first order rate of 0.03 per day. Removal of a BTEX compound was estimated by multiplying the rate of discharge of circulated water by the portion of the total mass that partitioned to the circulated water.

7

Estimate of bioremediation

The actual behavior of benzene is depicted in figure 4. The solid line is the calculated equilibrium concentration of benzene in the recirculation water, based on partitioning between ground water and JP-4 and on the rate of discharge of the circulated water. The connected dots are concentrations in the recirculation well that captured the greatest portion of infiltrated water. Concentrations rose slowly over time, overshot the prediction at about two recirculation volumes, then showed good agreement with the prediction for another recirculation volume.

Then biological acclimation occurred, and benzene was removed from the circulated water. Concentrations dropped below the analytical detection limit over a two-day period. Concentrations other BTEX compounds were not reduced (compare data for o-xylene in Figure 5), which established that the removal was a biological process. Notice from Figure 4 that removal of benzene occurred before nitrate was added to the system. This effect had not been predicted in the laboratory treatability study conducted as part of the design of the pilot scale demonstration (Hutchins et al. 1991).

CRITERIA FOR SUCCESS AT FIELD SCALE

The criteria for success at each remediation site are unique, depending on the particular requirements of State and Federal regulators, and the particular concerns of the site owner. However, requirements at many sites can be generalized to the following:

1) Concentrations of substances of regulatory concern in ground water will be less than the clean up goals established by the regulatory authorities at the end of active bioremediation.

2) Concentrations of substances of regulatory concern in ground water will not rise above the clean up goals, within a prescribed period of monitoring, after active bioremediation is concluded.

3) The site owner will enjoy beneficial use of his property during remediation, and will be allowed to sell or transfer the property when remediation is complete.

The following considerations have a direct bearing on the first two considerations.

Can Any Oily Phase Residual Support a Plume?

Monitoring wells can provide a misleading picture of the course of bioremediation. Pumping, or seasonal changes in regional water tables, can drop ground water elevations below the depth interval occupied by oily phase contaminants. Water produced by monitoring wells may be clean, but contamination will return when pumping stops, or recharge raises the regional water table elevation. Changes in the stage of nearby rivers or lakes, combined with seasonal variations in recharge, may alter the slope of the water table (hydraulic gradient), which will change the trajectory of the plume of contamination. Plumes may actually move away from monitoring wells under these conditions, then return to them at a later time.

To supplement data from monitoring wells, many regulatory authorities require a measure of residual oily-phase material left after bioremediation. Clean up goals are usually set with the conservative assumption that the relative composition of oily phase material does

not change during remediation. As a result, concentrations of oily-phase material that are determined to be protective of ground water quality are low, in the order of 10 to 100 mg Total Petroleum Hydrocarbon per kilogram aquifer material (Bell, 1990).

Bioremediation, and particularly innovative bioremediation that uses an electron acceptor other than oxygen, can remove the compounds of regulatory concern from the subsurface while leaving significant amounts of oily-phase hydrocarbons. The issue is whether any residual oily-phase hydrocarbon is capable of producing a plume of contamination at concentrations that exceed the clean up goal.

The JP-4 bioremediation demonstration at Traverse City Michigan was used to evaluate the importance of partitioning of contaminants between ground water and residual oily material. The concentration of BTEX compounds in recirculated ground water were compared to concentrations in the weathered oily phase residual.

When infiltration with nitrate brought the concentrations of BTEX compounds in the JP-4 spill below action levels, infiltration was stopped and concentrations of BTEX compounds in the aquifer were measured under natural conditions. Concentrations remained below action levels (Table I).

The JP-4 contaminated interval was cored, and analyzed for residual total hydrocarbons and concentrations of BTEX compounds. The reduction in concentration of Total Petroleum Hydrocarbons was minimal, from 2000 mg/kg to 1400 mg/kg, but the concentrations of BTEX compounds were reduced several orders of magnitude (Hutchins et al., 1991b). The concentration of BTEX compounds in the residual oil were divided by the fuel-to-water partition coefficients of Smith et al. (1981), to predict the capacity of the

10

residual to contaminate ground water. The concentrations predicted from the BTEX content of the oily residual were near or below the concentrations in monitoring wells under natural conditions of ground water flow (Hutchins et al. 1991b, see Table I).

Apparently ground water quality is controlled by the relative concentration of organic contaminants in the weathered oily phase residual, and not by the absolute amount of weathered total petroleum hydrocarbons. The relative concentration of organic contaminants can be used to predict the concentrations in ground water in contact with the oily-phase residual.

Accounting for Spatial Heterogeneity

Bioremediation is difficult to assess in heterogeneous geological material. Often, oily phase material is associated with fine textured material with low hydraulic conductivity. Remedial fluids tend to pass around the fine textured material. Because the flux of nutrients and electron acceptor through the fine textured material is small, there is little opportunity for bioremediation, and significant concentrations of contaminants can remain in subsurface material.

These relationships will be illustrated in a case history from an industrial site in Denver, Colorado (Nelson et al., 1993). A temporary holding tank under a garage leaked used crankcase oil, diesel fuel, gasoline, and other materials into a shallow water table aquifer. Figure 6 shows the relationship between the garage, the work pit containing the leaking holding tank, and the approximate area of the spill.

Remediation involved removal of separate oily phases, in-situ bioremediation with hydrogen peroxide and mineral nutrients, and bioventing. Ground water flow under ambient

11

conditions was to the North or Northeast. The flow of water during the remediation paralleled the natural gradient. Water was produced from a recovery well on the northeast side of the spill. The flow from the well was split; part of the flow was amended with hydrogen peroxide and nutrients and recharged to the aquifer in a nutrient recharge gallery on the south side of the spill (Figure 6). The remainder of the flow was delivered to a ground water recharge gallery located to the south of the nutrient recharge gallery. From 3 to 6 gpm was delivered to the nutrient recharge gallery, and 4 to 8 gpm was delivered to the ground water recharge gallery for a total flow of 9 to 11 gpm. Figure 7 presents a mathematical model of the flow paths from the galleries to the recovery well. The system was designed to sweep the ground water containing hydrogen peroxide and mineral nutrients through the spill to the recovery well.

The system was operated from October 1989 to March 1992. At a flow of 10 gpm, from ten to fifteen pore volumes would have been exchanged in the area between the nutrient recharge gallery and the recovery well.

Remediation of ground water in a case study

Table II compares the reduction in concentration of benzene and total BTEX compounds in ground water that was achieved by in situ bioremediation at the site in Denver. Examine figure 6 to locate the wells. Monitoring wells MW-1 and MW-8 are in areas with oily phase hydrocarbons. Well MW-2A is just outside the region with oily phase hydrocarbon. Well MW-3 is a significant distance from the region with oily phase hydrocarbon; it sampled the plume of contaminated ground water that moved away from the

12

spill. Prior to remediation, concentrations in wells MW-1 and MW-8 were equivalent. Well MW-1 was closest to the nutrient recharge gallery, and the aquifer surrounding MW-1 was completely remediated; BTEX compounds were undetectable in ground water. In well MW-8, immediately adjacent to the point of release, the concentration of benzene was reduced at least one order of magnitude, and the concentration of benzene and BTEX compounds in well MW-3 were also reduced an order of magnitude.

It is of particular interest that significant concentrations of benzene or total BTEX never developed in the pumped recovery well (RW-1), (reference to be supplied). The BTEX compounds were monitored twice a month from July 1989 to March 1992. Benzene was detected only once, at a concentration of 2 ug/liter. The other BTEX compounds were never detected. Water from contaminated flow paths sampled by MW-3 were probably diluted by uncontaminated water from other flow paths to RW-1 (compare Figure 7). This behavior illustrates the contrast in contaminant concentration between passive monitoring wells and pumped wells.

Remediation of subsurface material in a case study

Water in the monitoring wells and the recirculation well contained low concentrations of contaminants by March, 1992. Active remediation was terminated and the site entered a period of post remediation monitoring.

In June 1992 core samples were taken from the aquifer to determine the extent of hydrocarbon contamination remaining, and to determine whether a plume of contamination could return once active remediation ceased. The site was cored along a transect down gradient of the release. The transect extended laterally from clean material, through part of

the spill, into clean material on the other side (figure 6). In each borehole, continuous cores extended vertically from clean material above the spill, through the spill to clean material below. The cores were extracted and analyzed for Total Petroleum Hydrocarbons and for the concentration of individual BTEX compounds.

The relationship between the land surface, the water table, the region containing hydrocarbons, and the bed rock are presented in Figure 8. Significant amounts of hydrocarbons remain within a narrow interval approximately 2.0 feet thick, near the water table. The total saturated thickness of the aquifer was approximately 20 feet. At the time of sampling the elevation of the water table was 5280.5 feet above mean sea level (AMSL), and all the hydrocarbons were below the water table.

The highest concentrations of hydrocarbons at the site in Denver were obtained in samples from borehole D, which was closest to the source of the release, the work pit. Table III presents the vertical distribution of BTEX compounds and TPH in borehole D. The material in the interior of the spill had higher proportions of BTEX compounds. Table IV makes the same comparison at the most contaminated depth interval along the transect. Material closer to the spill had higher concentrations of TPH and greater relative proportions of BTEX compounds.

Figure 9 plots percent of BTEX in the residual oil after bioremediation against the total content of hydrocarbon. Obviously, the material with lower residual concentrations of hydrocarbons are more extensively weathered. Infiltration of hydrogen peroxide and mineral nutrients at an aviation gasoline spill in Michigan preferentially removed BTEX compounds from the oily phase gasoline, leaving a TPH residual low in aromatic hydrocarbons (Wilson et

14

al., 1992). Apparently at the Denver site, a cortex of material that has been physically and biologically weathered surrounds a central core of material that has not been depleted of BTEX compounds.

The concentration of an individual petroleum hydrocarbon in solution in ground water in contact with oily phase hydrocarbon can be predicted by Raoult's law. The solution concentration in water should be proportional to the mole fraction of the hydrocarbon in the oily phase. Assume that moving ground water is in contact with the weathered residual, but is not in effective contact with unweathered material. If partitioning between moving ground water and the weathered oily residual controls the concentration of hydrocarbons in the water, the ten-fold reduction in concentration of benzene and BTEX compounds seen in the weathered core material (table III) would produce the ten-fold reduction in concentration of benzene and BTEX compounds seen in the monitoring wells (Table II).

Do Mass Transfer Effects Limit Development of a Plume?

The usual expectation for in situ bioremediation is total removal of the contaminant from the subsurface environment. The extent of remediation that is most commonly achieved is removal of the contaminant from the circulating ground water.

In situ bioremediation merely accelerates the natural physical and biological weathering processes that occur in the subsurface. The oily material in most intimate contact with the circulated ground water is weathered to the greatest extent. After extensive remediation of the more transmissive regions, the release of contaminants to the circulated

ground water is controlled by difussion and slow advection from subsurface material that still contains significant quantities of contaminants. These relations are presented schematically in figure 10.

In such circumstances, the disposition of contamination in the ground water can only be understood as a dynamic system. As the circulated water passes through the weathered spill a certain quantity of hydrocarbon is transferred to the water. This transfer can be described through the chemical engineering concept of a mass transfer coefficient: the amount transferred is directly proportional to exposure time of the water in the contaminated area. If the circulated water contains enough nutrients and electron acceptor to meet the demand of the contaminants transferred from the fine textured material, the plume will be destroyed by biological activity as rapidly as it is produced. If the electron acceptor demand is greater than the supply, the plume will presist under active remediation, or be regenerated under ambient conditions.

When active remediation is stopped, the concentration of electron acceptor returns to ambient conditions in the aquifer, and the hydraulic gradient returns to the normal condition. As a result, the residence time of water in the spill area is longer, and the total amount of hydrocarbon transferred to the water is greater, although the supply of electron acceptor for biological destruction of the hydrocarbon is less (compare panels C and D in figure 10).

The relationships are well illustrated by the performance of bioremediation at the Denver site. During active bioremediation at the Denver site, the recharge water contained 1,000 mg/liter hydrogen peroxide, equivalent to 470 mg/liter molecular oxygen. During active remediation, the hydraulic gradient between the gallery and recovery well was 0.097.

16

The hydraulic conductivity in the depth interval containing the hydrocarbons is approximately 28 feet per day (Personal Communication David Szlag, University of Colorado, Boulder). Assuming an effective porosity of 0.35, this predicts an interstitial flow velocity of 7.8 feet per day. If the area with oily phase material is 150 feet in diameter, recirculated ground water would require 20 days to perfuse the spill, and could support an oxygen demand of approximately 20 mg per liter per day without depleting oxygen in the recirculating ground water.

Ambient ground water in the aquifer contains at most 5.5 mg/l oxygen. The hydraulic gradient just prior to start up of the demonstration was 0.0012, predicting an interstitial flow velocity of 0.1 foot per day. The natural flow of ground water would take 1,500 days to perfuse the spill, and could support an oxygen demand of 0.004 mg per liter per day without depleting oxygen.

In June, 1992, core material from the spill was assayed for its potential to consume oxygen. Core material was dewatered under a slight vacuum, then sealed in a glass mason jar. After twenty four hours, a sample of air in contact with the core material was passed through an oxygen indicating tube to estimate oxygen consumption. Acclimated material exerted oxygen demands of 6 to greater than 36 mg per kg core material per day (Table V), equivalent to 40 to greater than 240 mg per liter water per day. At these rates, the oxygen supplied as hydrogen peroxide could be consumed in two to twelve days.

In the assay, the microbes consumed oxygen faster than the oxygen was being supplied during active remediation. If the microbes in the aquifer expressed the potential rate of oxygen consumption, oxygen would have been depleted before the recharge water moved

across the spill. In the absence of oxygen, BTEX compounds would have partitioned to the ground water, and should have been detected in the monitoring wells. Oxygen consumption must have been limited by mass transfer of hydrocarbon to the circulating ground water.

Relationship to Siting and Sampling Monitoring Wells

If a plume regenerates because the supply of electron acceptor is not great enough to accept the hydrocarbon transferred to the moving ground water, it may require long periods of time to regenerate. Assuming mass transport limitations, transfer of hydrocarbon to ground water is proportional to residence time of ground water in the presence of the residual hydrocarbon. Ground water moving under the natural gradient must be allowed to travel all the way through the spill, then to the monitoring wells, before it is possible to determine whether mass transfer effects will reestablish a plume of ground water contamination.

An assessment of natural hydrologic conditions at a site will be necessary to intelligently locate compliance monitoring wells, and determine an appropriate schedule of monitoring. Required are an understanding of the average natural hydraulic gradient, and the hydraulic conductivity in the depth interval containing residual hydrocarbon. The frequency of monitoring should be related to the expected time required for ground water to travel through the area containing residual hydrocarbon to the point of compliance.

Table I. Comparison of concentrations of BTEX compounds in ground water before and after bioremediation of a JP-4 jet fuel spill to the concentration expected from dilution and from the BTEX content of the residual petroleum hydrocarbons.

Compound	Concentration prior to Bioremediation	Concentration predicted from Dilution	Concentration after Bioremediation	Concentration predicted from Residual
	-------------(ug/ liter)------------			
Benzene	760	262	<1	2
Toluene	4,500	900	<1	15
Ethylbenzene	840		6	6
m,p-Xylene	2,600		23	27
o-Xylene	1,380	400	37	18

Table II. Reduction in concentration of hydrocarbon contaminants in ground water achieved by in situ bioremediation of a spill from an underground storage tank.

Well	Benzene			Total BTEX		
	Before	During	After	Before	During	After
	m	----(ug/liter)---				
MW-1	220	<1	<1	2,030	164	<6
MW-8	180	130	16	1,800	331	34
MW-2A	?	11	0.8	?	1,200	13
MW-3	11	5	2	1,200	820	46
RW-1	<1	2	<1	<1	2	<1

Table III . Vertical extent of Total BTEX compounds and Total Petroleum Hydrocarbons after bioremediation of a spill from an underground storage tank. Cores are from borehole D, the most contaminated borehole in a transect across the spill (Figure 6).

Elevation	TPH	BTEX	Benzene	Color and Texture
(feet AMSL)	--(mg/kg)--			
281.14 to 5280.31	<44	<1	<0.2	Brown sand
5280.31 to 5279.97	227	5.1	<0.2	Brown sand
5279.97 to 5279.56	860	101	<0.2	Black sand
5279.56 to 5279.14	1176	206	4.3	Black sand
5279.14 to 5278.97	294	27	0.68	Black sand
5278.97 to 5278.64	273	7.4	0.26	Black sand
5278.64 to 5278.22	<34	<1	<0.2	Black sand
5278.22 to 5277.14	<24	<1	<0.2	Brown to yellow sand

Table IV. Lateral distribution of Total BTEX Compounds and Total Petroleum Hydrocarbons after bioremediation of a spill from an underground storage tank. The core are from the most contaminated depth interval along a transect (figure 6) across the spill.

Bore Hole	TPH	BTEX	Benzene
	--(mg/kg)--		
B	167	0.8	<0.2
C	156	3.5	<0.2
D	1,176	260	4.3
E	156	3.5	0.06

Table V. Oxygen demand of aquifer material after bioremediation of a spill from an underground storage tank, showing the relationship between the potential oxygen uptake rate of freshly collected core material and the location of the core material with respect to the depth interval contaminated with hydrocarbons.

Location in Borehole	Position of Borehole in the Transect					
	A	B	C	D	E	F
	--(mg oxygen per kg per day)---					
Just Above			<4		7.4	
Within	15.5	>30	>36		>34	23.5
Just Below	6.0	<3	5.7	7.3		21

REFERENCES

Bell, C.E. 1990. State-by-state summary of cleanup standards. Soils: analysis, monitoring, remediation, November-December 1990. Pp.10-16.

Downs, W.C., S.R. Hutchins, J.T. Wilson, R.H. Douglas, and D.J. Hendrix. 1989. Pilot project on biorestoration of fuel-contaminated aquifer using nitrate: Part I - Field design and ground water modeling. Pp. 219-133 in Proceedings, Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection, and Restoration. Houston, Texas, November 15-17, 1989. Dublin, Ohio. National Water Well Association.

Downs, W.C., S.R. Hutchins, J.T. Wilson, R.H. Douglas, and D.J. Hendrix. 1993. Nitrate-mediated biodegradation of BTEX in JP-4 contaminated soil and ground water. In: Flathman, P.E., D.E. Jerger, and J.H. Exner, Editors. Bioremediation: Field Experiences. In Press. Lewis Publishers, Chelsa, MI.

Hutchins, S.R., G.W. Sewell, D.A. Kovacs, and G.A. Smith. 1991a. Biodegradation of aromatic hydrocarbons by aquifer microorganisms under denitrifying conditions. Environmental Science & Technology 25(1):68-76.

Hutchins, S.R., W.C. Downs, J.T. Wilson, G.B. Smith, D.A. Kovacs, D.D. Fine, R.H. Douglass, and D.J. Hendrix. 1991b. Effect of nitrate addition on biorestoration of fuel-contaminated aquifer: Field demonstration. Ground Water 29(4):571-580.

Kampbell, D.H., and M.L. Cook. 1992. Core assay method for fuel contamination during drilling operations. Pp. 139-140 in Subsurface Restoration Conference Proceedings, National Center for Ground Water Research, Rice University, P.O. Box 1892, Houston, Texas.

Kennedy, L.G., and S.R. Hutchins. 1992. Applied Geologic, Microbial, and Engineering Constraints of In-Situ BTEX Bioremediation. Remediation 3(1):83-108.

Nelson, C., R.J. Hicks, and S.D. Andrews. 1993. In-situ bioremediation: an integrated system approach. In: Flathman, P.E., D.E. Jerger, and J.H. Exner, Editors. Bioremediation: Field Experiences. In Press. Lewis Publishers, Chelsa, MI.

Robbins, G.A., R.D. Bristol, and V.D. Roe. 1989. A field screening method for gasoline contamination using a polyethylene bag sampling system. Ground Water Monitoring Review, Fall 1989. Pp. 87-97.

Siegrist, R.L., and P.D. Jenssen. 1990. Evaluation of Sampling Method Effects on Volatile Organic Compound Measurements in Contaminated Soils. Environmental Science and Technology 24(9):1387-1392.

Smith, J.H., J.C. Harper, and H. Jaber. 1981. Analysis and environmental fate of Air Force distillate and high density fuels. Engineering and Services laboratory, Air Force Engineering and Services Center, Tyndall Air Force Base, Fl. Report ESL-TR-81-54.

Zapico, M.M., S. Vales, and J.A. Cherry. 1987. A wireline piston core barrel for sampling cohesionless sand and gravel below the water table. Ground Water Monitoring Review 7(3):74-82.
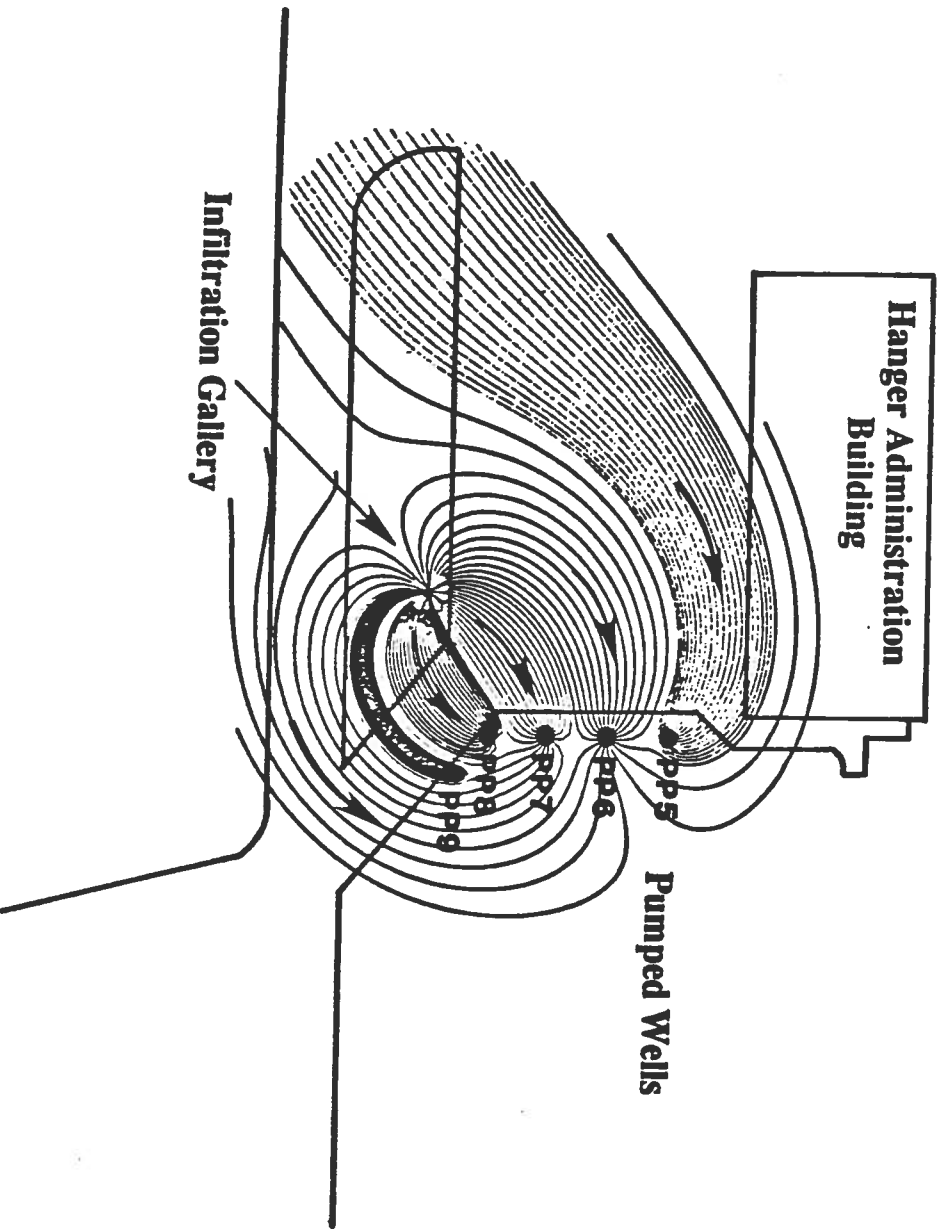
Hanger Administration Building

Infiltration Gallery

Pumped Wells

PP9 PP8 PP7 PP6 PP5

100 M

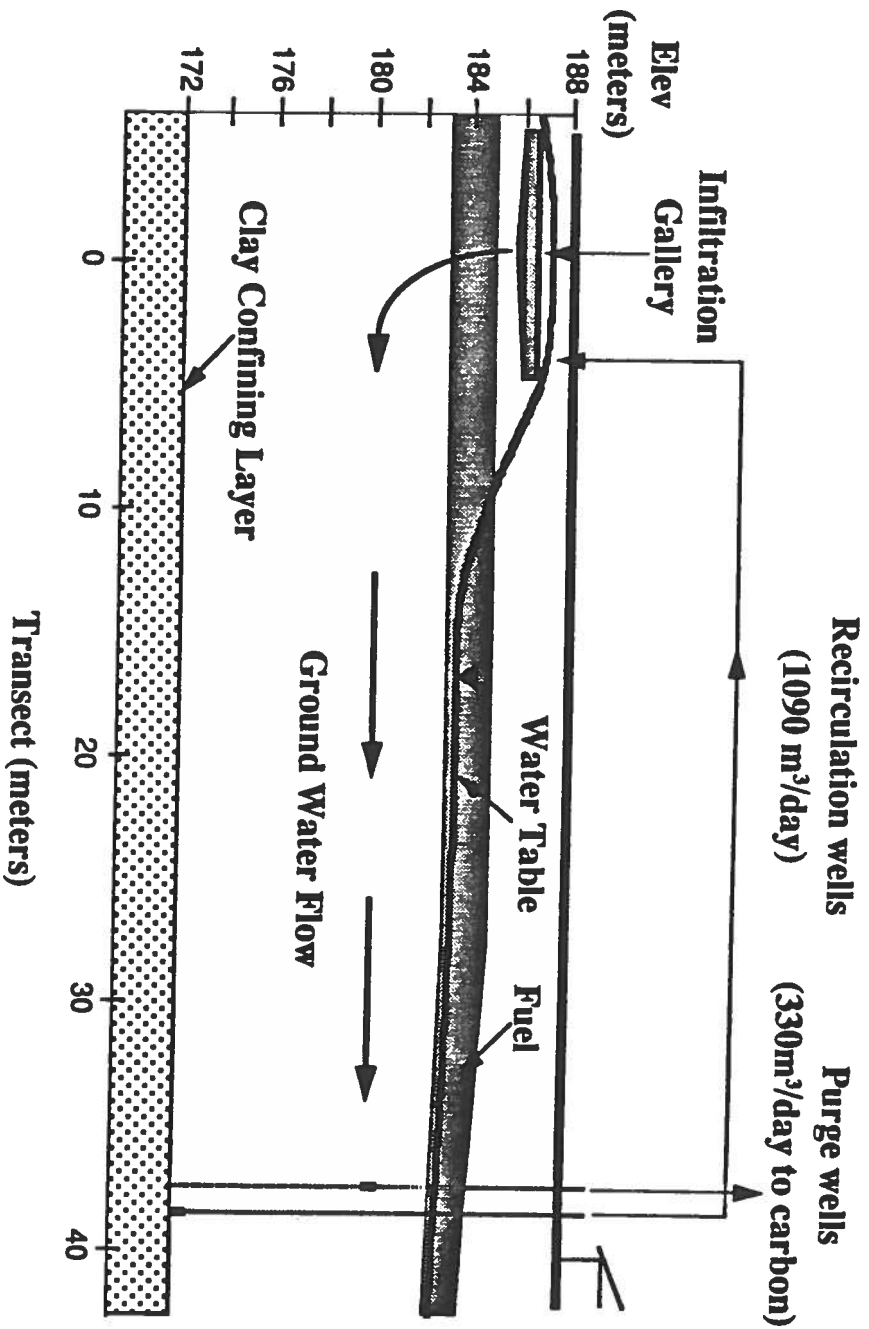Figure 1. Hydraulic model of in situ bioremediation of a JP-4 spill at the Traverse City Demonstration Site. Ground water amended with mineral nutrients and nitrate as an electron acceptor was recharged through an infiltration gallery. The model predicted flow lines from the infiltration gallery to pumping wells (PP5 to PP9) that capture and recirculate ground water. To capture the infiltrated water containing nitrate, more water was pumped than was delivered to the gallery. As a result, some of the flow lines to the wells originate in uncontaminated ground water upgradient of the spill.

Figure 2. Cross section of a JP-4 spill at the Traverse City Demonstration Site. Ground water amended with mineral nutrients and nitrate as an electron acceptor. Water was recirculated to an infiltration gallery installed above the JP-4 spill. It moved vertically across the spill, then laterally through the aquifer to the recovery wells. Part of the recovered water was recirculated, part was purged.
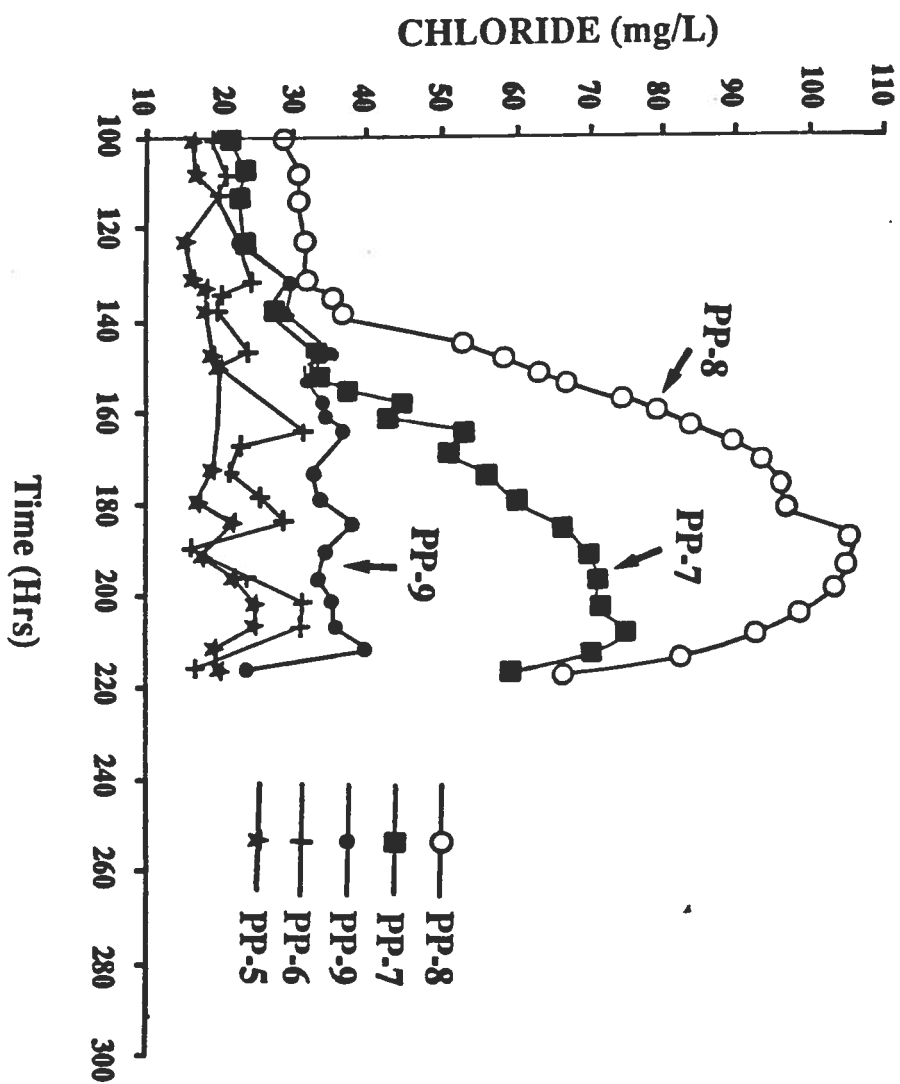
Figure 3. Breakthrough of chloride from a tracer test conducted to evaluate the hydraulic model of water flow. Chloride was added to water supplied to the infiltration gallery. The concentration of chloride that breaks through to pumped wells should be proportional to flow along lines that originate in the infiltration gallery, compared to flow along lines that originate upgradient in the aquifer. Compare Figure 1 for flow lines and location of pumped wells.
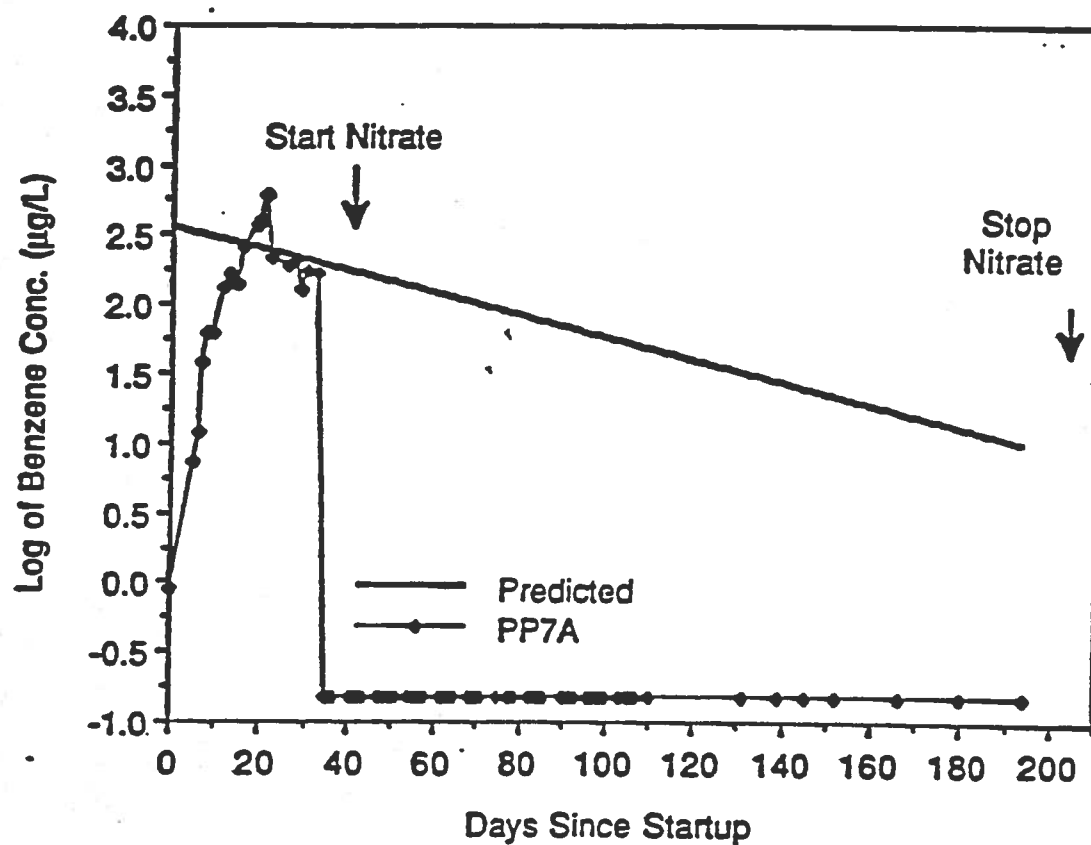
Daily Benzene Levels

FIGURE 4 Bioremediation of a JP-4 jet fuel spill using nitrate. Comparison of the depletion of benzene in circulated ground water, to the depletion predicted from dilution and partitioning.
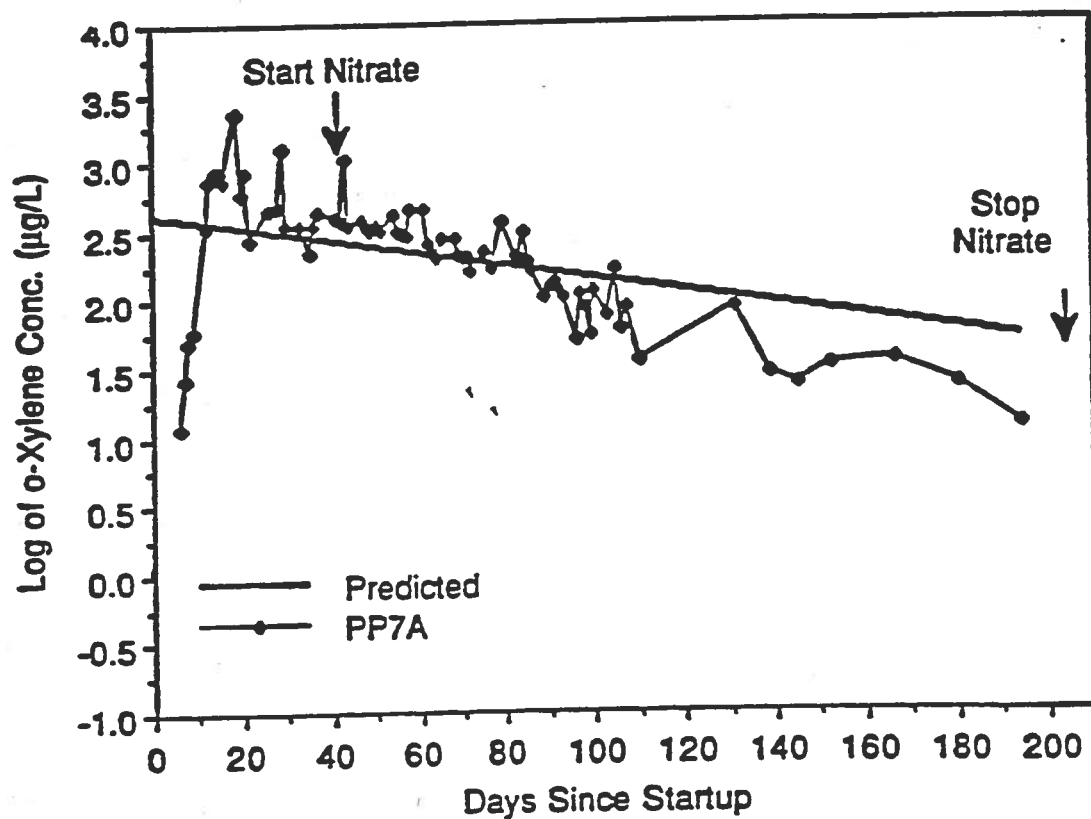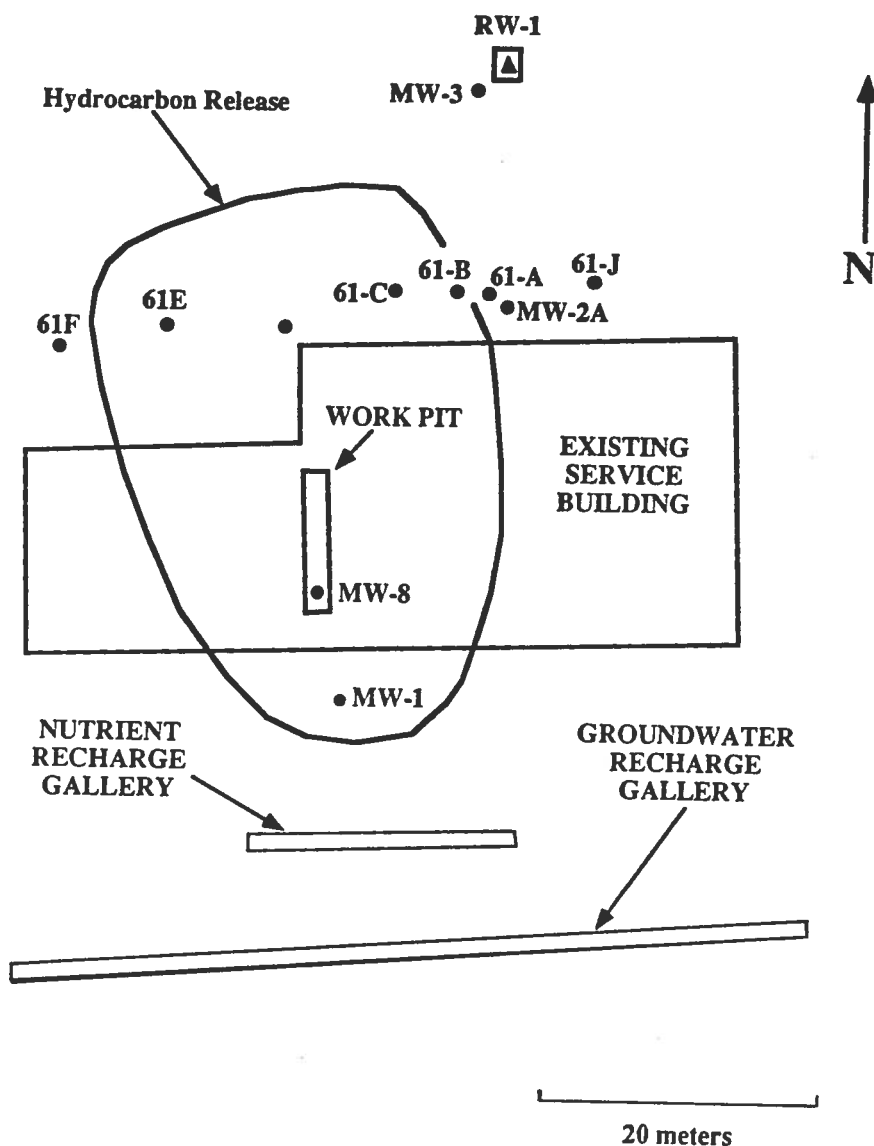
Daily o-Xylene Levels

FIGURE 5 Bioremediation of a JP-4 jet fuel spill using nitrate. Comparison of the depletion of o-Xylene in circulated ground water, to the depletion predicted from dilution and partitioning.

Figure 6. Infrastructure at an in situ bioremediation project at Denver Colorado. A holding tank in a work pit under a garage leaked petroleum hydrocarbons to the water table aquifer. Ground water was pumped from a recovery well (RW-1) and filtered through activated carbon. The flow was split, part was amended with hydrogen peroxide and mineral nutrients, and recharged in a nutrient recharge gallery. The remainder was recharged in a ground water recharge gallery. The system was designed to sweep hydrogen peroxide and nutrients under the service building. MW-1, 2A and 3 are monitoring wells. 61A through 61J are boreholes for cores.
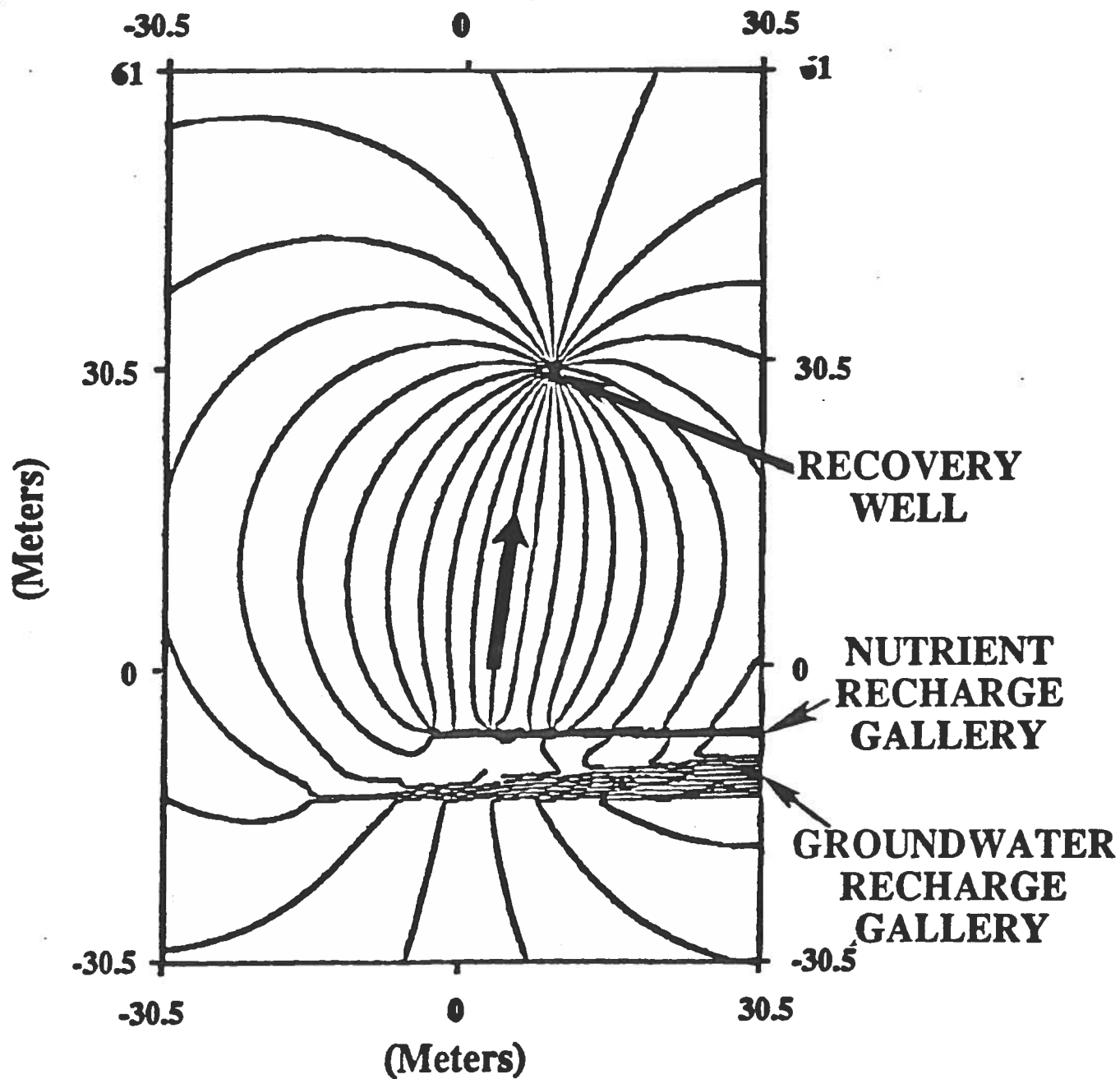
Figure 7. Hydraulic model of flow from the nutrient recharge gallery to the recovery well. Notice that the spill is contained within the flow path from the gallery to the well, and that the well captures all the flow lines from the nutrient recharge gallery.

Elevation (feet AMSL)

A   B   C   D   E   F

5300
5290
Clay
5280
Source of Hydrocarbons
Sand
Clay
5270
Water Table
Residual Hydrocarbon
Sandy Aquifer
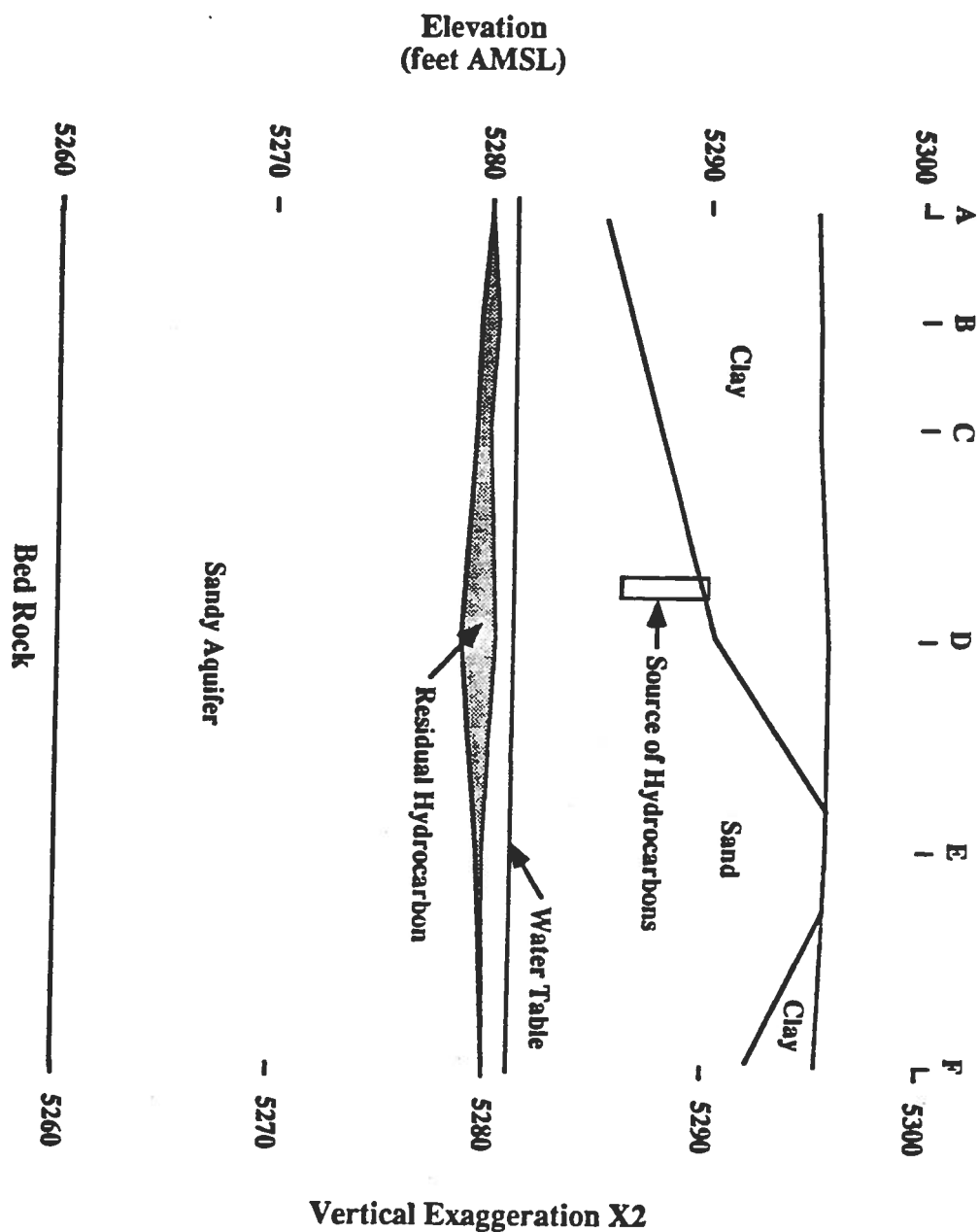5260
Bed Rock

Vertical Exaggeration X2

Figure 8. Cross section showing the vertical relationship of the land surface, water table, residual hydrocarbon remaining after bioremediation, and the lower confining layer of the aquifer. The cross section runs through core boreholes depicted in figure 6.
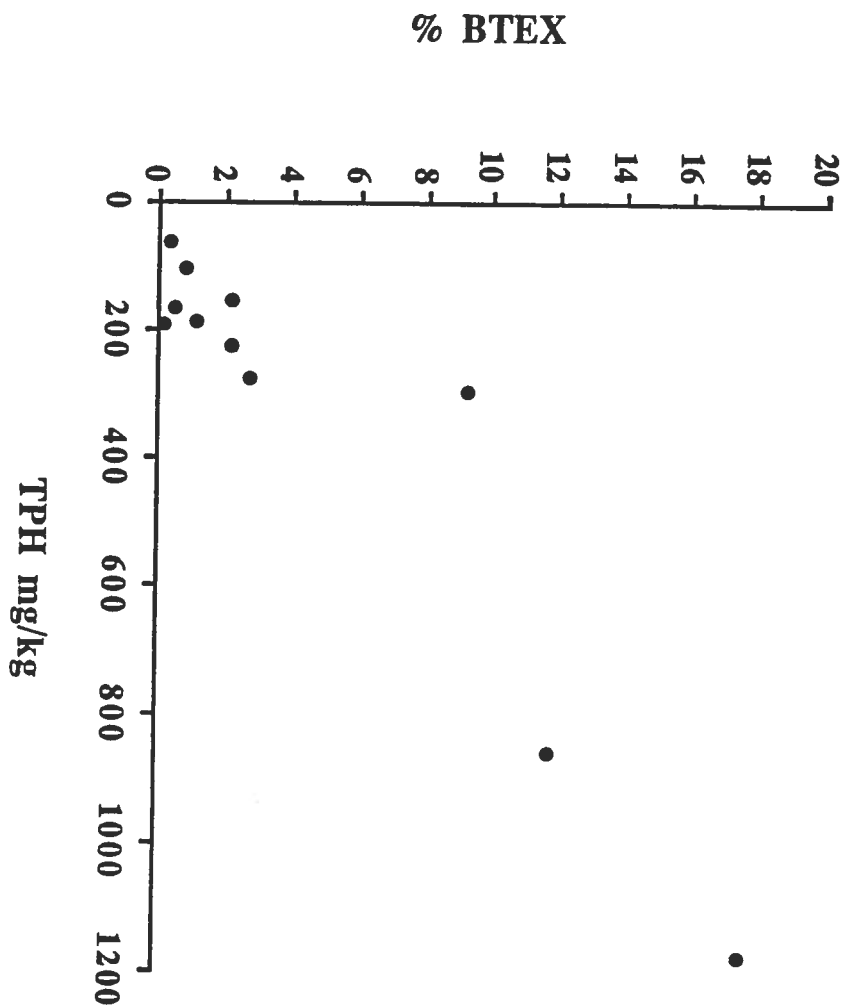
Figure 9. Relationship between extent to hydrocarbon contamination (concentration of total petroleum hydrocarbons) and the extent of biological and chemical weathering (reduction in percent BTEX compounds in total petroleum hydrocarbons) in core material after bioremediation at the Denver Site.
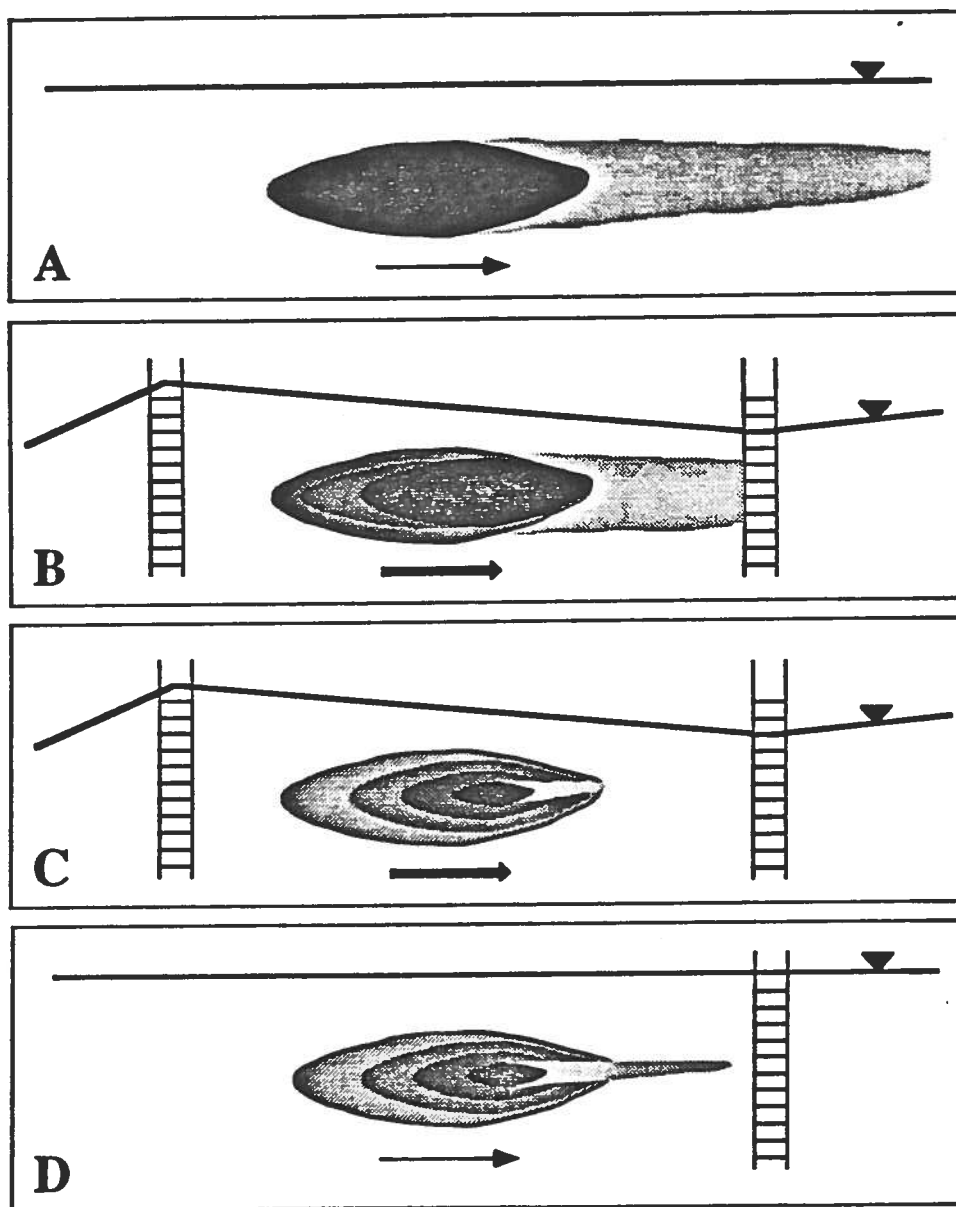
FIGURE 10. Schematic representation of in situ bioremediation in heterogeneous geological material. A fresh release (panel A) is rapidly weathered (panel B) due to increased flow of water and increased concentration of electron acceptor. As weathering progesses, aromatic hydrocarbons such as the BTEX compounds are restricted to regions with low hydraulic conductivity (panel C). After bioremediation the flux of aromatic hydrocarbons from the residual core to moving ground water is controlled by mass transport limitations. The extent of the plume produced is controlled by the supply of electron acceptor (panel D). Although greatly attenuated, the plume may be regenerated under ambient conditions.